

Layer silicate clays – Genesis and classification

Genesis of Clay Minerals

The silicate clays are developed from the weathering of a wide variety of minerals by the two distinct process

1. Alteration- A slight physical and chemical alteration of certain primary minerals.

Changes in particle size. Alteration of muscovite mica to fine grained mica is the good example. As weathering occurs muscovite mineral is broken down in size to the colloidal range, part of the potassium is lost and some silicon is added from weathering solutions. Net result is the less rigid crystal structure and an electronegative charge. The fine mica colloid has a 2:1 structure, only have been altered in this process

2. Recrystallization- Decomposition of primary minerals with subsequent recrystallization of certain of their products in to the silicate clays

Complete breakdown of clay structures and re-crystallization of clay minerals from product of this breakdown. It is the result of much more intense weathering than that required for alteration. Formation of Kaolinite (1;1) from solutions containing soluble aluminum and silicon that came from the breakdown of the primary minerals having 2;1 type structure

Relative stages of weathering

Weathering

The contact of rocks and water produces clays, either at or near the surface of the earth” (from Velde, 1995).

Rock + Water → Clay

The CO₂ gas can dissolve in water and form carbonic acid, which will become hydrogen ions H⁺ and bicarbonate ions, and make water slightly acidic.



The acidic water will react with the rock surfaces and tend to dissolve the K ion and silica from the feldspar. Finally, the feldspar is transformed into kaolinite.

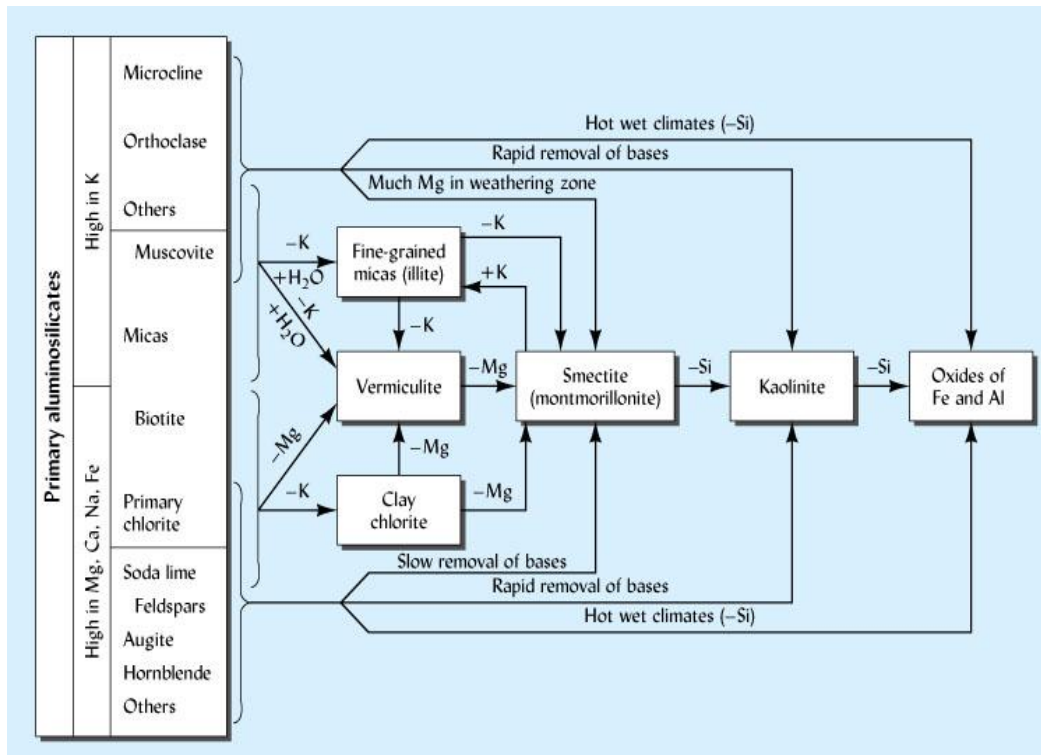
Feldspar + hydrogen ions + water → clay (kaolinite) + cations, dissolved silica



Fine grained micas and magnesium rich chlorites represent earlier weathering stages of the silicates and kaolinite and ultimately iron and aluminum oxides the most advanced stages

Genesis of individual clays

Figure: General conditions for the formation of the various layer silicate clays and oxides of iron and aluminum. Fine-grained micas, chlorite, and vermiculite are formed through rather mild weathering of primary aluminosilicate minerals, whereas kaolinite and oxides of iron and aluminum are products of much more intense weathering. Conditions of intermediate weathering intensity encourage the formation of smectite. In each case silicate clay genesis is accompanied by the removal in solution of such elements as K, Na, Ca, and Mg.



1. Layer silicate clays

These important silicate clays are also known as phyllosilicates (Phyllon - leaf) because of their leaf-like or plate like structure. These are made up of two kinds of horizontal sheets. One dominated by silicon and other by aluminum and/or magnesium.

Silica tetrahedron: The basic building block for the silica-dominated sheet is a unit composed of one silicon atom surrounded by four oxygen atoms. It is called the silica tetrahedron because of its four-sided configuration. An interlocking array or a series of these silica tetrahedra tied together horizontally by shared oxygen anions gives a tetrahedral sheet.

Alumina octahedron: Aluminium and/or magnesium ions are the key cations surrounded by six oxygen atoms or hydroxyl group giving an eight sided building

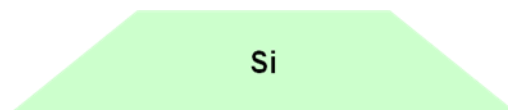
block termed octahedron. Numerous octahedra linked together horizontally comprise the octahedral sheet.

An aluminum-dominated sheet is known as a di-octahedral sheet, whereas one dominated by magnesium is called a tri-octahedral sheet. The distinction is due to the fact that two aluminum ions in a di-octahedral sheet satisfy the same negative charge from surrounding oxygen and hydroxyls as three magnesium ions in a tri-octahedral sheet.

The tetrahedral and octahedral sheets are the fundamental structural units of silicate clays. These sheets are bound together within the crystals by shared oxygen atoms into different layers. The specific nature and combination of sheets in these layers vary from one type of clay to another and control the physical and chemical properties of each clay.

Tetrahedral & Octahedral Sheets

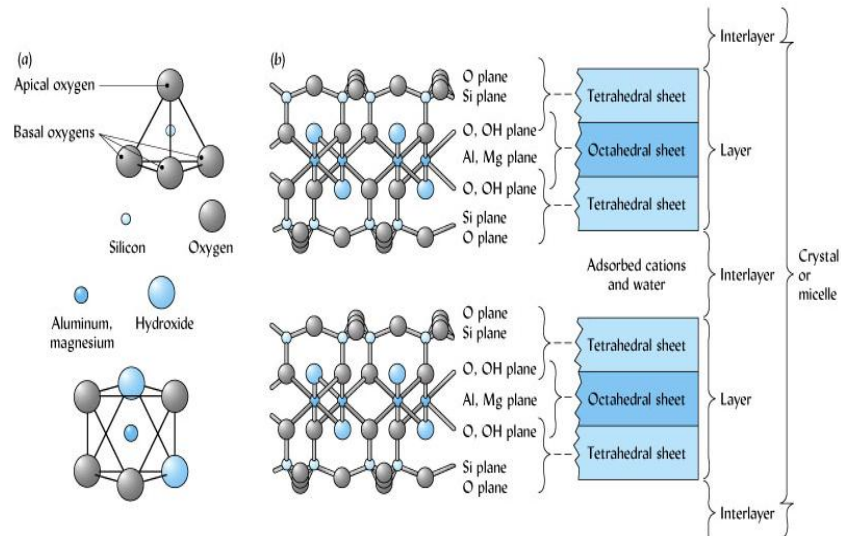
For simplicity, let's represent **silica tetrahedral** sheet by:



and **alumina octahedral** sheet by:



The building blocks and structural components of silicate clays



Classification of layer silicate clays

On the basis of the number and arrangement of tetrahedral (silica) and octahedral (alumina-magnesia) sheets contained in the crystal units or layers, silicate clays are classified into three different groups

- 1) 1 :1 Type clay minerals
- 2) 2:1 Type clay minerals
- 3) 2: 1: 1 (or) 2:2 Type clay minerals

The basic building blocks of tetrahedral and octahedral sheets are the silica tetrahedron and the aluminum octahedron

The Si^{4+} cation occurs in fourfold and tetrahedral coordination with oxygen while the Al^{3+} is generally found in six fold or octahedral coordination

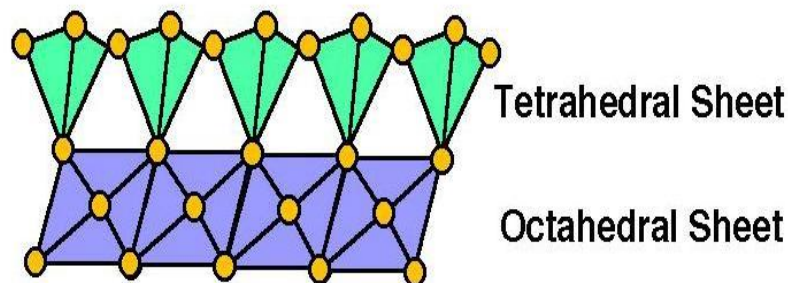
Layer silicate minerals are sometimes defined on the basis of the number of certain positions occupied by cations. When two-thirds of the octahedral positions are

occupied, the mineral is called dioctahedral; when all 3 positions are occupied it is called trioctahedral.

1:1 type minerals

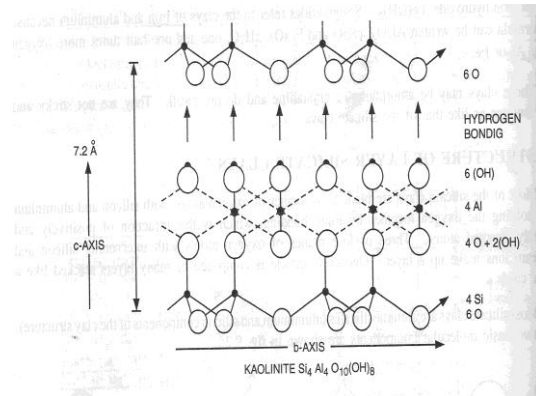
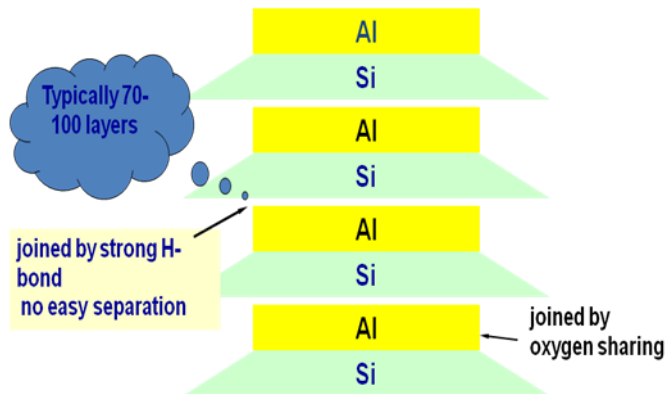
The layers of the 1:1-type minerals are made up of one tetrahedral (silica) sheet combined with one octahedral (alumina) sheet. In soils, **kaolinite group** is the most prominent 1:1 clay mineral, which includes kaolinite, hallosite, nacrite and dickite. The tetrahedral and octahedral sheets in a layer of a kaolinite crystal are held together tightly by oxygen atoms, which are mutually shared by the silicon and aluminum cations in their respective sheets. These layers, in turn, are held together by hydrogen bonding. Consequently, the structure is fixed and no expansion ordinarily occurs between layers when the clay is wetted.

Cations and water do not enter between the structural layers of a 1:1 type mineral particle. The effective surface of kaolinite is restricted to its outer faces or to its external surface area. Also, there is little isomorphous substitution in this 1:1 type mineral. Because of low surface area and little isomorphous substitution the capacity to adsorb cations is also low.



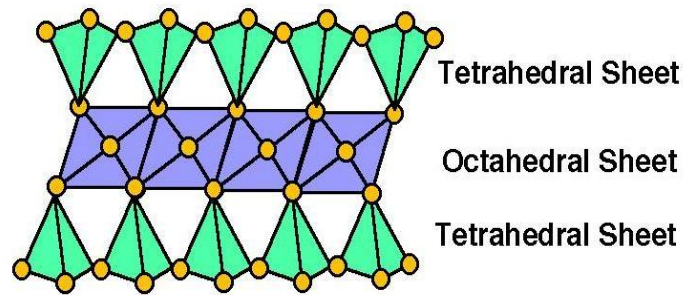
Kaolinite crystals usually are hexagonal in shape. In comparison with other clay particles, they are large in size, ranging from 0.10 to 5 μm across with the majority falling within the 0.2 to 2 μm range. Because of the strong binding forces between their structural layers, kaolinite particles are not readily broken down into

extremely thin plates. Kaolinite exhibits very little plasticity (capability of being molded), cohesion, shrinkage, and swelling.



2:1-Type Minerals

The crystal units (layers) of these minerals are characterized by an octahedral sheet sandwiched between two tetrahedral sheets. Three general groups have this basic crystal structure.

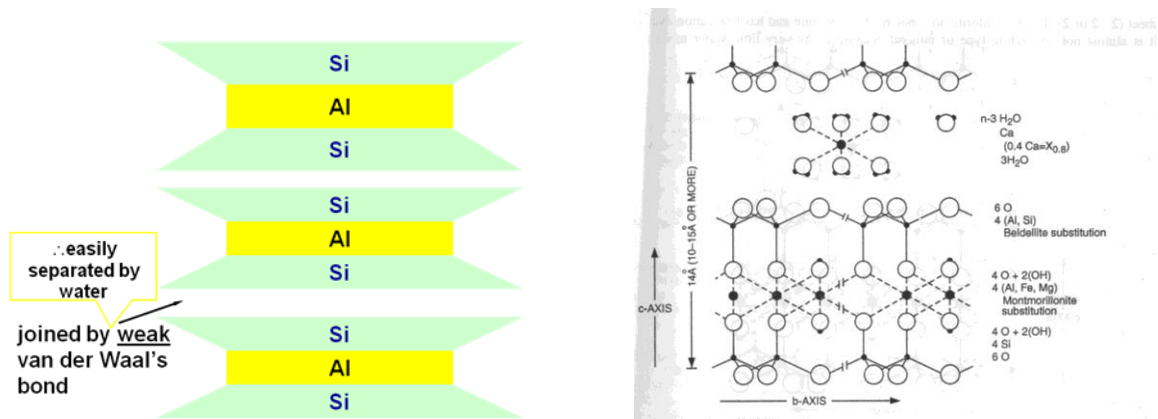


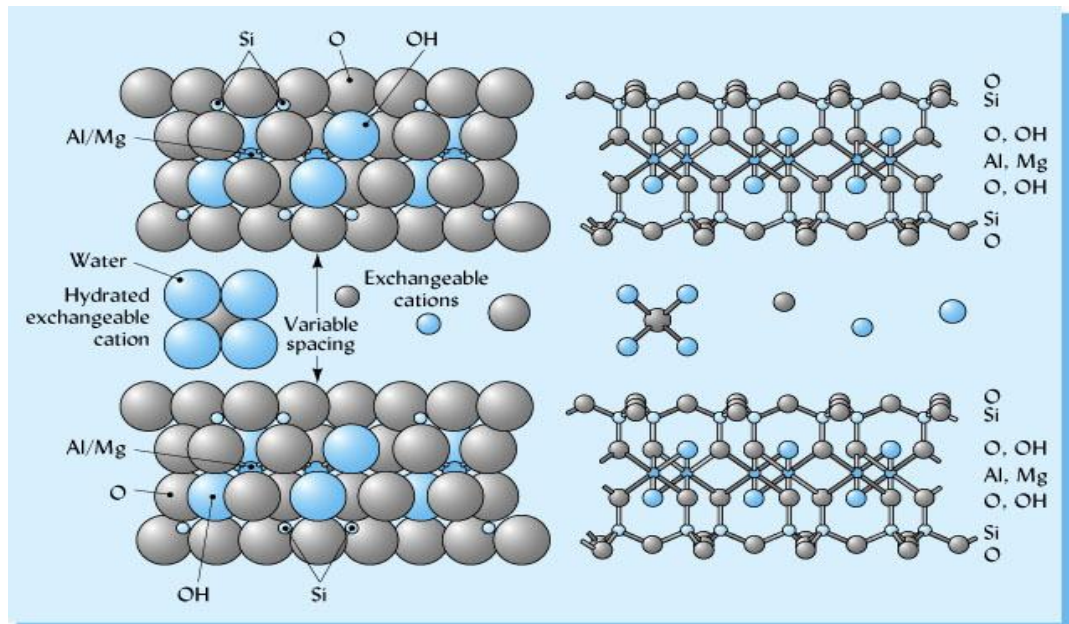
- Expanding type: Smectite group and vermiculite
- Non-expanding type: mica group (illite)

Expanding Minerals: The smectite group of minerals is noted for their interlayer expansion and swelling when wetted. The water enters the interlayer space and forces the layers apart. Montmorillonite is the most prominent member of this group in soils. Beidellite, nontronite, and saponite are also found in soils.

The flake-like crystals of smectite (e.g., **Montmorillonite**) are composed of an expanding lattice 2:1 type clay mineral. Each layer is made up of an octahedral sheet sandwiched between two tetrahedral (silica) sheets. There is little attraction between oxygen atoms in the bottom tetrahedral sheet of one unit and those in the top tetrahedral sheet of another. This permits a ready and variable space between layers, which is occupied by water and exchangeable cations. This internal surface exceeds the external surface of clay crystal. In montmorillonite, magnesium replaces aluminum in some sites of octahedral sheet. Likewise, some silicon atoms in the tetrahedral sheet may be replaced by aluminum. These substitutions give rise to a negative charge.

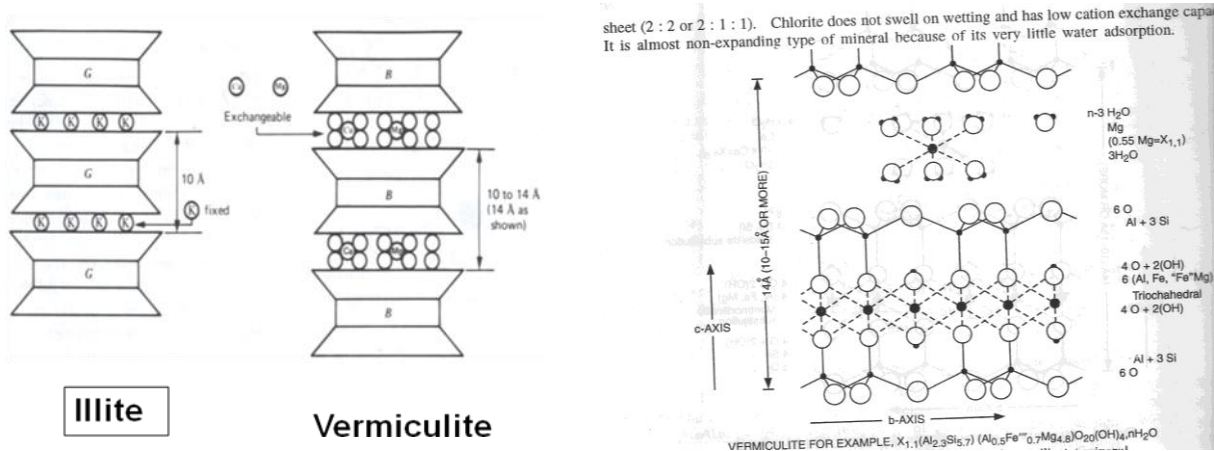
These minerals show high cation exchange capacity, swelling and shrinkage properties. Wide cracks commonly form in smectite dominated soils (e.g., Vertisols) when dried. The dry aggregates or clods are very hard, making such soils difficult to till.



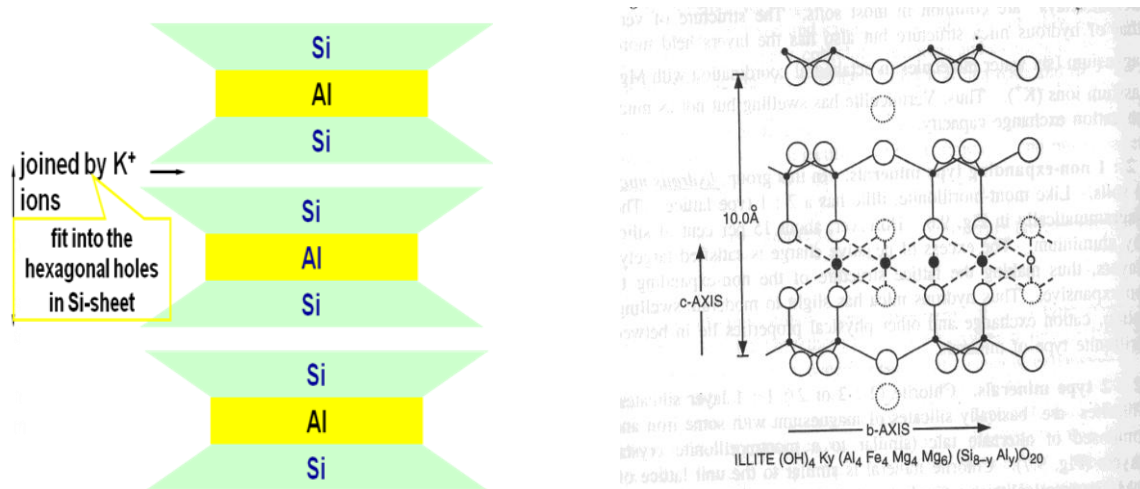


Vermiculites are also 2:1 type minerals in that an octahedral sheet occurs between two tetrahedral sheets. In most soils vermiculites, the octahedral sheet is aluminum dominated (di-octahedral), although magnesium dominated (tri-octahedral) vermiculites are also present. In the tetrahedral sheet of most vermiculite, aluminum is substituted by silicon in most of the sites. This accounts for most of the very high net negative charge associated with these minerals. Water molecules, along with magnesium and other ions, are strongly adsorbed in the interlayer space of vermiculites. They act primarily as bridges holding the units together rather than as wedges driving them apart. The degree of swelling is, therefore, considerable less for vermiculites than for smectite. For this reason, vermiculites are considered limited expansion clay minerals, expanding more than kaolinite but much less than the smectite. The **cation exchange capacity** (CEC) of vermiculite is higher than all other silicate clays, including montmorillonite and other smectite because of very high negative charge in the tetrahedral sheet. Vermiculite crystals are larger than those of the smectite but much smaller than those of kaolinite.

Structure of vermiculite



Structure of illite



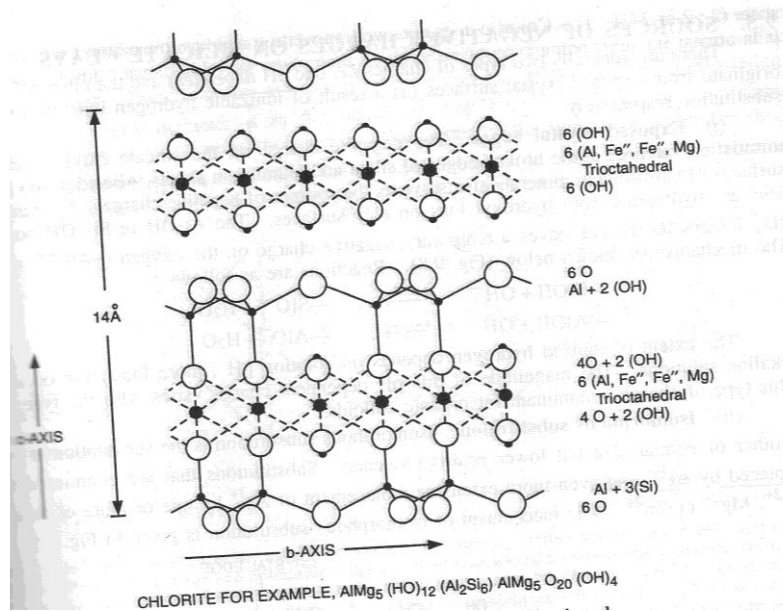
2:1 Non-expanding minerals: Micas are the type minerals in this group. (e.g.) Muscovite and biotite. Weathered minerals similar in structure to these micas are found in the clay fraction of soils. They are called fine-grained micas. Like smectite, fine-grained micas have a 2:1 type crystal. However, the particles are much larger than those of the smectite. Also, the major source of charge is in the tetrahedral sheet where aluminum atoms occupy about 20% of the silicon sites.

This results in a net negative charge in the tetrahedral sheet and the charge is higher than that found in vermiculites. To satisfy this charge, potassium ions are strongly attracted in the interlayer space and are just the right size to fit into spaces in the adjoining tetrahedral sheets. The potassium thereby acts as a binding agent, preventing expansion of the crystal. Hence, fine-grained micas are quite non-expanding.

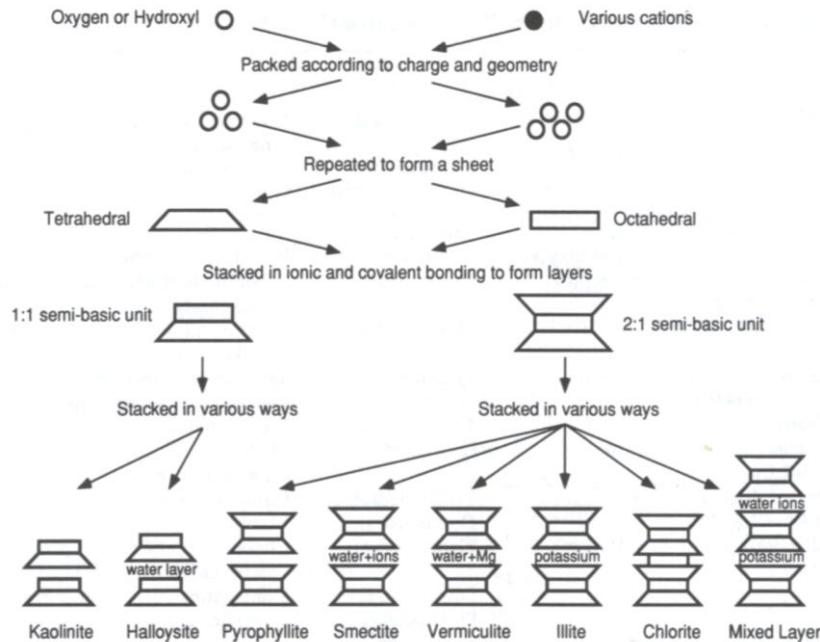
The properties such as hydration, cation adsorption, swelling, shrinkage and plasticity are less intense in fine grained micas than in smectite but are more than kaolinite due to the presence of interstratified layers of smectite or vermiculite. Fine grained mica crystals are intermediate in size between the smectite and kaolinite. Their specific surface area varies from 70 to 100 m² g⁻¹, about one eighth that for the smectite.

2:1:1 Type Minerals: This silicate group is represented by **chlorites**. Chlorites are basically iron magnesium silicates with some aluminum present. In a typical chlorite clay crystal, 2:1 layers, such as in vermiculites, alternate with a magnesium dominated tri-octahedral sheet, giving a 2:1:1 ratio. Magnesium also dominates the tri-octahedral sheet in the 2:1 layer of chlorites. Thus, the crystal unit contains two silica tetrahedral sheets and two magnesium-dominated tri-octahedral sheets giving rise to the term 2:1:1 or 2:2 type structure.

The negative charge of chlorites is about the same as that of fine grained mica and less than smectite or vermiculites. Like fine micas, chlorites may be interstratified with vermiculites or smectites in a single crystal. Particle size and surface area for chlorites are also about the same as for fine grained micas. There is no water adsorption between the chlorite crystal units, which accounts for the non expanding nature of this mineral.



Mixed and interstratified layers: Specific groups of clay minerals do not occur independently of one another. In a given soil, it is common to find several clay minerals in an intimate mixture. Furthermore, some mineral colloids have properties and composition intermediate between those of any two of the well defined minerals described. Such minerals are termed mixed layer or interstratified because the individual layers within a given crystal may be of more than one type. Terms such as "chlorite-vermiculite" and "mica - smectite" are used to describe mixed layer minerals. In some soils, they are more common than single structured minerals such as montmorillonite.



2. Iron and aluminum oxide clays (sesquioxide clays): Under conditions of extensive leaching by rainfall and long time intensive weathering of minerals in humid warm climates, most of the silica and alumina in primary minerals are dissolved and slowly leached away. The remnant materials, which have lower solubility are called sesquioxides. Sesquioxides (metal oxides) are mixtures of aluminum hydroxide, $\text{Al}(\text{OH})_3$, and iron oxide, Fe_2O_3 , or iron hydroxide, $\text{Fe}(\text{OH})_3$. The Latin word *sesqui* means one and one-half times, meaning one and one-half times more oxygen than Al and Fe. These clays can grade from amorphous to crystalline. Examples of iron and aluminum oxides common in soils are gibbsite ($\text{Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$) and goethite ($\text{Fe}_2\text{O}_3 \cdot \text{H}_2\text{O}$). Less is known about these clays than about the layer silicates. These clays do not swell, not sticky and have high phosphorus adsorption capacity.

Sesquioxide Clays (Metal Oxides and Hydrated Oxides)

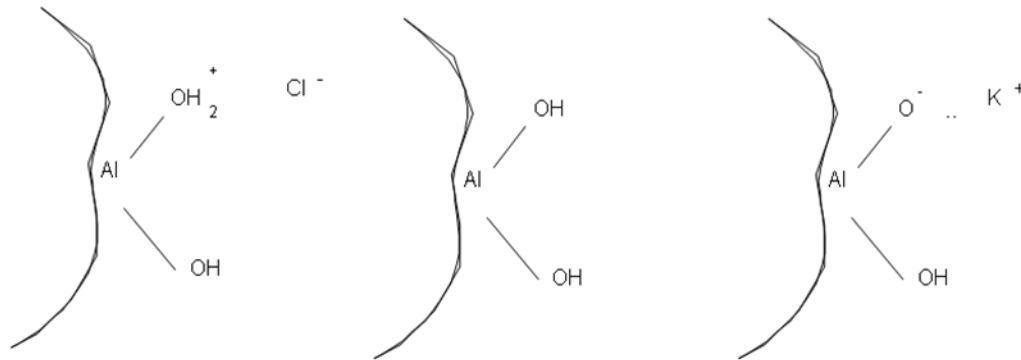
Also found in finer component. These tend to form in soils as Si is depleted by leaching. Gibbsite is the most common Al oxide mineral and is often found in

highly weathered soils such as oxisols in tropical areas and ultisols found predominantly in the southeastern U.S. The most common iron oxides are Goethite ($\text{FeO}(\text{OH})$) and Hematite (Fe_2O_3). These are also found in highly weathered soils and give many red soils their color. The metal oxides gibbsite and goethite tend to persist in the environment because Si is readily leached than Al, or Fe and a significant amount of soluble organic matter is present. Manganese oxides are also quite common in soils. Apart from being an essential plant nutrient, they are a natural oxidant to certain metals such as As^{3+} and Cr^{3+} . Birnessite (MnO_2) is the most common Mn oxide found in soils. Most of the charges developed on the metal oxides are pH-dependent.

Allophane and other amorphous minerals: These silicate clays are mixtures of silica and alumina. They are amorphous in nature. These are structurally disordered aluminosilicates. Typically, these clays occur where large amounts of weathered products exist. They are normally derived from volcanic ash materials and constitute a major component of volcanic soils. Allophane is often associated with clay minerals of the kaolinite group. Imogolite has the empirical formula $\text{SiAl}_4\text{O}_{10}\cdot 5\text{H}_2\text{O}$. These clays have high anion exchange capacity or even high cation exchange capacity. Almost all of their charge is from accessible hydroxyl ions (OH^-), which can attract a positive ion or lose the H^+ attached.

These clays have a variable charge that depends on H^+ in solution (the soil acidity).

Allophane, Fe and Al hydrous oxides are : they take on different charges depending upon pH.



Low pH (protonated, anion exchange site)

Zero Point of Charge

High pH (deprotonated, cation exchange site)

Carbonate and Sulfate Minerals

The carbonate and sulfate minerals are highly soluble compared to the aluminosilicates and are more prevalent in arid and semi arid regions. The major carbonate minerals are calcite ($CaCO_3$) and Dolomite ($CaMg(CO_3)_2$). The major sulfate mineral is gypsum.

Comparative properties of silicate clay minerals

Property	Montmorillonite	Illite	Kaolinite
Structure	2:1 lattice	2:1 lattice	1:1 lattice
	Substitution in octahedral sheet by Mg or Fe	Substitution in Tetrahedral sheet by Al	No Substitution
Shape	Irregular flakes	Irregular flakes	Hexagonal crystals
Total surface area (m^2g^{-1})	700-800	100-120	5-20

Cohesion Plasticity and swelling capacity	High	Medium	Low
External surface Internal surface	Very high	Medium	Not at all
Cation Exchange capacity	80-100	15-40	3-15
Anion exchange capacity	Low	Medium	High
